

Article

Fine Characterization of Co/Fe-Based Materials: Insights into the Influence of Cation Ratios Between 2/2 and 10/2 on Obtaining Layered Double Hydroxides

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Abstract

Co/Fe layered double hydroxides (LDHs) are among the most promising materials for advanced industrial and energy applications. Controlling the synthesis conditions of LDH materials is thus crucial to precisely tailoring cation composition and distribution, thereby regulating surface charge, ion sorption, and electron transfer required for optimal chemical and electrochemical performance. Therefore, characterizing Co/Fe precipitates (chemical composition, purity, morphology, and crystallinity) is also required to further exploit their controlled properties. Thus, solids with Co/Fe cation ratios between 2/2 and 10/2 were synthesized under an air atmosphere, at pH 8 or 11.5. For the first time, multiscale physicochemical techniques (FTIR, TEM-EELS, SEM, AAS, TGA, CHN elemental analysis, and XRD complemented by Rietveld refinement) were used to provide a fully documented characterization of the structure, texture, purity, chemical composition, and thermal properties of Co/Fe LDH-based materials. The combined interpretation of data from these complementary techniques enabled the precise identification and chemical characterization of the mineralogical phases formed. Both acid–base and redox reactions govern the overall Co^{II}/Fe^{III} LDH formation process. Well-crystallized LDHs were synthesized, except for the 2/2 ratio at pH 11.5, which led to the formation of α -Co(OH)₂, γ -Fe₂O₃, and Co₃O₄ byproducts. A pH value of 8.0 provides valuable LDH materials made of quasi-hexagonal particles with diagonal lengths between 200 and 500 nm. Rietveld refining showed the presence of LDH phases in the range of 95–98%. Multiple local chemical analyses using EDX on chosen particles demonstrated pure 4/2 and 6/2 LDHs. For the 2/2 ratio, the cumulative mass fraction of two LDH-type products consistently reached 97%, distributed between Co/Fe 1.5/2 (71%) and Co/Fe 4/2 (29%). For the 10/2 ratio, only partial Co precipitation was observed, forming 95% Co/Fe LDH phases distributed between Co/Fe 10/2 (72%) and 7/2 (28%).

Keywords: layered double hydroxides; Co/Fe ratio; co-precipitation synthesis by varying pH; in-depth multiscale characterization



Received: 19 December 2025

Revised: 5 February 2026

Accepted: 10 February 2026

Published: 24 February 2026

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1. Introduction

Layered Double Hydroxides (LDHs) consist of Brucite-like layers in which a fraction of divalent cations, occupying the centers of hydroxylated octahedra linked by their edges,

is primarily replaced by trivalent ones with similar radii, forming unlimited, positively charged sheets [1–4]. These sheets are linked to each other through electrostatic interactions and hydrogen bonding between positively charged sheets and hydrated interlayer anions, resulting in electro-neutrality by counterbalancing excess positive charge [5,6].

The general formula of LDHs is $[M_{(1-x)}^{II}M_x^{III}(OH)_2](A^{n-})_{\frac{x}{n}} \cdot mH_2O$, where M^{II} represents divalent cations (Mg^{2+} , Fe^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , etc.); M^{III} represents trivalent cations (Al^{3+} , Cr^{3+} , Mn^{3+} , Ga^{3+} , Fe^{3+} , etc.), with x the molar fraction of trivalent cations substituting the divalent cations ($x = M^{III}/(M^{III} + M^{II})$); A^{n-} represents interlayer anions (CO_3^{2-} , SO_4^{2-} , HCO_3^- , NO_3^- , Cl^- , F^- , AsO_4^{3-} , etc.); and m is the number of water molecules [3,4,7–13]. The presence of water in the interlayer space depends on the affinity of the intercalated anions towards the water molecules and the LDH layers, whose charge excess depends on isomorphic substitutions [14,15].

In LDHs, the Brucite-like layers usually crystallize with either rhombohedral or hexagonal symmetry [4,16]. The distance between two adjacent layers principally depends on the nature, hydration energy, and charge of the interlayer anionic species, as well as their electrostatic interaction with the layers [14,15,17]. Different polytypes can thus be observed based on the stacking sequence of the Brucite-like layers. Several methods have been performed for the synthesis of a broad range of particle sizes ($1\text{ nm} < d < 10\text{ }\mu\text{m}$) of LDHs with various chemistries, crystallinities, and morphologies [18–20], leading to a large spectrum of specific surface area values, up to $\sim 100\text{ m}^2/\text{g}$. The easiest and most common method is conventional co-precipitation at a constant pH value [21–25], although co-precipitation at a variable pH is also widely employed [5,19,26,27].

The synthesis pH value strongly influences the composition, crystallinity, morphology, and pore structure of LDHs [5,19,28]. For Al-based LDHs, crystallinity increases with pH above 10, while higher pH values lead to larger particle sizes and distinct morphological changes [19,29–31].

The modulation of the required $R = M^{II}/M^{III}$ ratio controls the charge density, which affects the anionic exchange capacity (AEC: $\text{mEq}/100\text{ g}$), ranging from 200 and $450\text{ mEq}/100\text{ g}$ for $0.20 < x < 0.33$ [18]. Furthermore, the nature and proportion of cations constituting the LDH layers influence the interlayer affinity of LDHs for anions [11,12,32,33]. This also influences the PZNC pH value and, consequently, the external surface charges responsible for anion or cation surface sorption phenomena [14,15,34]. Moreover, the use of redox active elements makes it ultimately possible to control, via the modulation of the excess of structural cationic charge, (i) the interlayer anion exchange capacity and/or (ii) anion and cation adsorption [14,15,34,35].

The nature of structural cations and interlayer anions largely determines the properties of LDHs, making them suitable for a wide range of industrial and environmental applications over the past three decades, including heterogeneous catalysis [26], optical materials [36,37], separation technology [38], flame retardants [39,40], ions exchangers [41,42], cement additives [43], drug delivery hosts [44], pharmaceutical uses [45,46], plastic resins stabilization [47], soil fertilizers [48–51], corrosion/protection [52,53], environmental applications [35,54–59], hydrometallurgy (pre-concentration of metals) [60], energy storage (development of batteries and supercapacitors) [61–71], photoelectrochemical applications [72], and breakthrough electrolysis processes for the capture or release of cations and/or anions [73].

In this sense, cobalt-based LDHs have been increasingly investigated since 2010 for electrochemical applications [5,35,57,67,69,74–80]; when introduced as trivalent cations, Fe^{III} ensures efficient electrical conductivity via electron transfer within the mineral structure [35].

A previous study [18] reported the formation of pure LDH phases predominantly at M^{II}/M^{III} molar ratios ranging from 4/2 to 6/2, highlighting the difficulty of obtaining pure

phases at lower or higher ratios. For Co/Fe LDHs, Gregoire et al. [81] showed that a cation ratio of 4/2 ($x = 0.33$) is the minimum that can be used to synthesize LDHs. Cavani et al. [18] suggested that, for lower ratios, some trivalent cations become first neighbors, potentially leading to a sensitive increase in the electrostatic repulsion in the cation layer [81]. For higher ratios, co-precipitation of LDH phases easily occurs due to the increasing distance between trivalent atoms carrying excess cationic charges. The authors of the study only completed the usual crystallographic characterization and global chemical analyses of the synthesized solids to determine the nature of the elaborated crystalline phases and the precipitated total metal content. The lack of subsequent complementary characterizations weakens their conclusions, not only with respect to ensuring LDH-type compounds were obtained, but also in determining their purity and chemical composition.

The development of Co/Fe-based LDH materials requires control over the mechanisms involved in their formation, as redox-active precursor elements are likely to interact with each other, along with dissolved dioxygen or water molecules [5]. Once physicochemical conditions have been established, it is crucial to finely characterize the synthesized solids in terms of mineralogical and crystallochemical properties, cation ratio, and morphology.

This study carefully characterizes Co/Fe-based materials obtained using the co-precipitation method with varying pH values for further insights into the influence of the cation ratio, from 2/2 to 10/2, on obtaining LDH phases. The influence of the cationic ratio on the successful formation of pure LDH phases was rigorously investigated. In addition to the global mineral and chemical composition of synthesized solids, for the first time, in all cases, the real chemical composition of LDHs was investigated and rigorously assessed: (i) Co/Fe, (ii) the M^{II}/M^{III} ratio, (iii) hydroxide content, (iv) anion nature, content and speciation, and (v) water content. This was performed based on morphological aspects. The formation of additional phases has also been detailed. For this purpose, this approach includes X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy coupled with electron energy loss spectroscopy (TEM/EELs), scanning electron microscopy (SEM), atomic absorption spectroscopy (AAS), CHN elemental analysis, and thermogravimetric analysis (TGA). Crossed comprehensive characterization techniques further emphasize the originality and significance of this work.

2. Experimental Section

2.1. Reagents

All chemicals (>99.8% purity) used for the acid–base titration of Co and Fe solutions were supplied by ACROS: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Na_2CO_3 , and NaOH. KBr (>99% purity, IR spectroscopy quality) used for FTIR measurements was supplied by Merck-Sigma-Aldrich (Darmstadt, Germany). Nitric acid (Fisher Chemicals (France), 65% purity) was used to dissolve solids prior to chemical analysis. MilliQ-water 18 M Ω used to prepare solutions was produced by the Merck Millipore Milli-Q® Direct 8 water purification system.

2.2. Protocol of Precipitation Pathway of Co and Fe via Acid–Base Titration

High supersaturation conditions were used in the Co and Fe coprecipitation pathway. This procedure involves adding an alkaline aqueous solution (2.80 M NaOH and 0.78 M Na_2CO_3) to a cationic solution containing various proportions of Co^{II} and Fe^{III} ($0.5 \leq x \leq 0.17$ with $x = M^{III}/[M^{III} + M^{II}]$; Table 1) by varying the pH until the desired value is reached. Syntheses were carried out considering a constant number of cations (0.18 moles). This study investigates the formation of conventional M^{II}/M^{III} ratio (4/2 and 6/2) LDHs. It also investigates two extreme ratios, 2/2 and 10/2, containing very low and very high amounts of Co, respectively.

Table 1. Co/Fe ratios and concentrations used to reach the targeted x ratios.

Co/Fe Molar Ratio	x = Fe/(Fe + Co) Molar Fraction	Cobalt Concentration (mol/L)	Iron Concentration (mol/L)
2/2	0.50	0.090	0.090
4/2	0.33	0.120	0.060
6/2	0.25	0.135	0.045
10/2	0.17	0.150	0.030

We performed alkaline titration to pH 11.5 for five cationic aqueous mixtures for which x values were chosen in a range of 0.5 to 0.17. We did so to (i) study the effect of adding an alkaline solution on the evolution of Co/Fe solution pH values and (ii) to select synthesis pH values. Two pH values (8.0 and 11.5) were investigated to explore the influence of these values on Co/Fe LDH crystallinity, morphology, and purity.

The titrant was added accurately under vigorous stirring (500 rpm). Titrations were conducted under an air atmosphere and atmospheric pressure in a thermoregulated 3 L cylindrical Pyrex double-walled water-jacketed reactor at 35 °C (DC10-P5/U thermostat bath, Haake, Vreden, Germany). During titrations, pH values were recorded as a function of time up to the highest pH value (11.5). pH values were measured using Exact450 Yokogawa (Tokyo, Japan), and the addition of alkaline solution was controlled by an MV1000 Yokogawa pH-control unit, leading to a variable alkaline solution flow rate.

During the material elaboration, since aging increases the crystallinity of LDHs, particularly the particle size, the suspensions were aged at 60 °C for 24 h; these temperature and duration values are commonly used in the literature [19,21,31,82,83].

After aging, solids and liquids were separated via centrifugation (CR4-12, 4500 rpm, 5 min, Jouan refrigerated centrifuge, Artisan Technology Group, Champaign, IL, USA). The precipitated Co/Fe solids were then dialyzed using a 1 M sodium carbonate solution to perform anion exchange. This treatment minimized the presence of nitrate and hydroxide anions, possibly introduced during co-precipitation. A MWCO 3.5 kD dialysis tubing membrane (Merck, Darmstadt, Germany) was used during the exchange process. The exchanged solids were then finally washed via dialysis in a deionized water bath, renewed every day for 5 days to remove extra salts.

The resulting Co/Fe-CO₃ solids were then dried at 40 °C for 24 h and finely ground using an agate mortar to obtain a fine powder for characterization.

2.3. Characterization Techniques

The obtained powder was fully characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), atomic absorption spectroscopy (AAS), thermogravimetric analysis (TGA), elemental analysis (CHNO), and gas adsorption measurements (BET).

XRD analyses were carried out on randomly oriented powder samples using a Bruker D8 Advance X-ray diffractometer (Palaiseau, France) equipped with Cu K α radiation ($\lambda = 1.54056$ Å), operating at 40 kV and 40 mA, and a fast multichannel LynxEye XE-T detector. Data were collected from 4 to 75° in 2 θ using a step size of 0.03° in 2 θ and a count time of 288 s per step.

Data treatment was carried out using DIFFRAC EVA V7.3 (Bruker, Karlsruhe, Germany), associated with the ICDD PDF5+ 2024 database. Quantitative analyses were carried out using TOPAS V.6 from Bruker (Germany). Quantification was based on Rietveld

refinement [84], which involves minimizing the sum of the weighted squares of the deviations between intensities from an experimental diffractogram and those of a theoretical diffractogram. The theoretical diffractogram was calculated from the crystallographic and structure data of the different phases of the samples, plus instrumental effects.

Over a range of $300\text{--}4000\text{ cm}^{-1}$, the FTIR spectra were recorded using an Equinox55 (Bruker, Germany) spectrometer using a transmission technique with a resolution of 4 cm^{-1} . This identified interlayer anions.

Potassium ferricyanide (Aldrich, Sheboygan Falls, WI, USA, 99%) was used as an internal standard to facilitate a semi-quantitative analysis of the Co/Fe solid IR spectra because its narrow intense peak—observed at 2100 cm^{-1} [85] corresponding to the CN^- group—does not interfere with LDH bands. To form solid pellets, 150 mg of KBr powder, 0.5 mg of solid, and 0.15 mg of internal standard were mixed before pellet creation.

The SEM observations were carried out on an FEG (Field Emission Gun, high resolution) SEM-type TESCAN Mira3XMU (Brno, Czech Republic) equipped with an EDS microanalysis system (energy-dispersive X-ray spectrometry, EDAX TEAM, SDD detector without liquid nitrogen EDAX XPP). Images were obtained under high vacuum, using a secondary electron detector “In Beam” (IBSE) at 10 kV, while EDS spectra were acquired at 15 kV. To make them conductive to a precise investigation of LDH morphology, the samples were covered with a 2 nm layer of platinum–palladium using the chemical vapor-deposition technique prior to analysis.

TEM analyses were carried out with a MET CM20 microscope (Philips: Field Electron and Ion Company, Hillsboro, OR, USA) operating at 200 kV. One drop of the suspension was deposited on the carbon membrane of the grid, and the solvent was evaporated at room temperature. High-resolution transmission electron microscopy was performed on a JEOL ARM 200CF (Tokyo, Japan) double corrected microscope at 80 kV and 200 kV, in high-resolution parallel mode and scanning mode. These techniques were used to examine the morphology and characterize the structure of the LDHs and secondary phases, when present. EDX/TEM analysis quantitatively determined the metal ratio (Co/Fe) of the observed particles.

EELS spectra were extracted from an EELS mapping area of $10\text{ nm} \times 10\text{ nm}$, acquired with a Quantum dual EELS Gatan spectrometer (Pleasanton, CA, USA). For statistical measurement, five areas were recorded. Each spectrum image was calibrated and denoised, and an average spectrum was extracted. HRTEM was performed to establish the mineralogical nature of the nanocrystallites, and EELS measurements were used to determine the iron redox state.

TGA was performed using STA 449-F5 Jupiter NETZSCH equipment (Selb, Germany) to investigate the degradation mechanism of the solids and to determine the number of physisorbed and intercalated water molecules present within the LDH structure. For this purpose, a 1-degree ramp per minute was applied from ambient temperature to $900\text{ }^\circ\text{C}$ under argon flow (50 mL/min).

Adsorption–desorption measurements of N_2 at 77 K (Figure S1) were performed on solids using gas manometry (Quantachrome, Autosorb LS123, Helmholtz. Berlin, Germany). The measurements were carried out after degassing the samples at $80\text{ }^\circ\text{C}$ under vacuum (10^{-2} mbar) over 72 h (Figure S1). From the isotherm data, the specific surface area was calculated by applying the BET equation in a P/P_0 range of 0.05 to 0.3. By fitting the isotherm curve using the DFT equation (slit pore, NLDFE equilibrium model), the micropores ($0.7\text{--}2\text{ nm}$) and mesopores ($2\text{--}50\text{ nm}$) volumes were evaluated.

AAS analyses (Varian AA 200 Varian, Inc. Grenoble, France) ($\lambda_{\text{Fe}}\text{ }372\text{ nm}$ and $\lambda_{\text{Co}}\text{ }240.7\text{ nm}$) were performed on both slurries, and precipitates were mineralized in nitric acid medium to investigate the Co/Fe ratios. A micropipette was used to sample 1 mL of Co/Fe

solid slurry, which was then added to 9 mL of nitric acid (Aldrich, 65% purity). For solids, 20 mg of the samples were dissolved in 20 mL of nitric acid (Aldrich, 65% purity). Prior to analysis, after complete dissolution of the solids, the solution was successively filtered using 0.45 μm and 0.1 μm filters (Sodipro, Échirolles, France, Nylon, $d = 13\text{ mm}$).

Elemental analysis (CHON analysis) of C, H, N, and O was performed using flash pyrolysis (900–950 $^{\circ}\text{C}$), followed by quantification of evolved gases (FLASH 2000 CHNS/O: Thermo Fisher Scientific Inc., Les Ulis, France). Cysteine was used as the standard. This analysis was used complementarily to EDX, IRTF, and TGA to determine the crystallochemistry of LDH solids in terms of the chemical composition of the cationic layers, interlamellar anion speciation (carbonates, hydrogen carbonates, and/or nitrates), and hydration level, using the mass content determination of each element.

2.4. LDH Chemical Formula Calculation

Realistic Co/Fe LDH structures were determined using a combination of AAS elemental analyses (Varian AA 200 Varian, Inc., Grenoble, France), XRD refinement, and stoichiometry determined by local analysis (TEM/EDX). Combining the Co/Fe EDX ratio with the initially introduced Co/Fe value and the nature and content of the crystalline phase determined by XRD analysis allowed us to define the molar content of Co, Fe, O, and H in the crystalline phases. Then, using CHON results, the nature and speciation of the LDH interlamellar anions (CO_3^{2-} , HCO_3^- , NO_3^-) were determined. Finally, residual hydrogen moles were implemented to define the LDH hydration level. More details of the methodology are given in Supplementary Information S3.

3. Results and Discussion

3.1. Synthesis Conditions and Characterization of Elaborated Co/Fe Solids

Before any fine characterization of synthesized solids, the physical and chemical conditions influencing the formation of LDHs were investigated to maximize the formation of LDH phases.

3.2. Determination of pH Values Favoring Co/Fe LDH Formation

The acid/base titration was performed by adding an alkaline aqueous solution to mixed Co/Fe solutions in high supersaturation conditions for different Co/Fe solution ratios. This allowed us to obtain the curves shown in Figure 1.

As dissolved Fe^{3+} ions behave as a “weak Lewis acid”, the higher the initial Fe solution content, the lower the starting pH value. When adding the first drops of alkaline titrant to the metallic cation solution, pH increases slowly, in agreement with H^+ consumption through reaction with OH^- . This H^+ consumption is also linked to the protonation of CO_3^{2-} , yielding HCO_3^- and then H_2CO_3 [5]. Due to the pH increase, Fe^{3+} hydrolysis begins, inducing the simultaneous formation of $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$. The first plateau was noticed at a pH value between 2.4 and 3 and was related to Fe^{III} precipitation as ferrihydrite, in agreement with Morcos et al. [5]. The continuously modulated addition of alkaline solution increases the suspension’s pH value; this reaches a second plateau in a pH range of 6.5–7.5, where Co/Fe LDH co-precipitation is expected to occur [5]. Notably, the drift in the pH value is used to control the addition of the alkaline solution. Thus, we could not calculate the quantity of alkaline reagents introduced during each titration step, mainly linked to the consumption of reagents through the neutralization of protons and the precipitation of introduced metallic species. Figure 1 illustrates the plateau magnitudes linked to Fe precipitation, Co/Fe LDH co-precipitation, and the co-precipitation of Co/Fe LDHs. The higher the Fe content, the lower the Co content, the longer the duration of the

Fe precipitation plateau, and (therefore) the shorter the Co/Fe co-precipitation plateau duration, and vice versa.

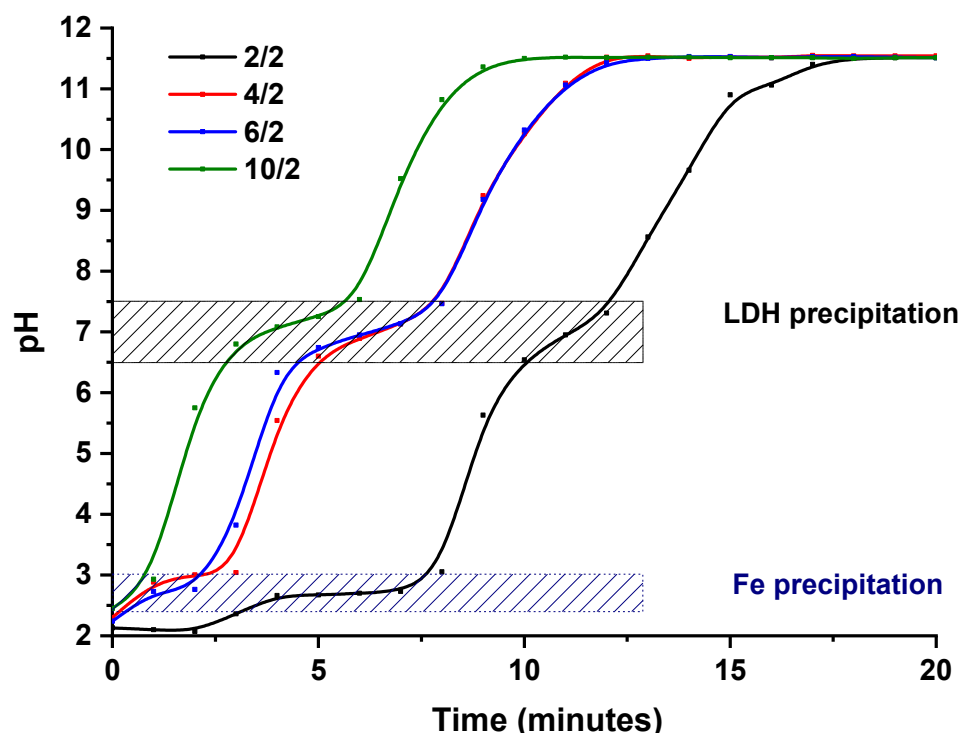


Figure 1. Acid–base titration curves of $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ solutions using NaOH and Na_2CO_3 solutions.

Co-precipitation of cobalt and iron starts at a pH value around 6.5 and slows down at pH 7.5. Consequently, an initial LDH synthesis pH value of 8.0 was chosen to ensure the highest LDH precipitation rate. In the present work, synthesis was also performed at a pH value of 11.5, as publications have shown that increasing the pH value induces an increase in the crystallinity of some LDH compositions [19,30,31]. The third plateau, at a pH of 11.5, agreed with the pH of the alkaline solution used to titrate Co/Fe solutions and synthesize LDHs.

3.3. Crystallinity and Purity of Co/Fe Solids

Figures 2a and 2b show diffractograms of the matured Co/Fe- CO_3 solids elaborated at pH values of 11.5 and 8.0, respectively.

Except for the solid obtained by titrating the 2/2 Co/Fe ratio solution to a pH value of 11.5, whatever the synthesis pH value, strong and narrow diffraction peaks were observed at 2θ values of 11; 23, 34; 38.5; 59; and 61° , which are characteristic of the (003), (006), (012), (015), (110), and (113) families of reticular Co/Fe- CO_3 LDH plans [5,86–88] (JCPDS 04-017-8816). The peaks appearing at medium angles—between 2θ and 30 to 50° , corresponding to the h0l and 0kl positions—depend on the polytype and were affected by stacking defects. The XRD peaks of the synthesized Co/Fe LDH were characteristic of a mixture of rhombohedral 3R-1 and 3R-2 polytypes [89,90]. Indeed, the two polytypes show similar reflections at the same XRD positions and can only be distinguished using the intensity of the h0l and the 0kl reflections. The 3R-1 polytype was characterized by strong 0kl reflections, while the 3R-2 polytype exhibits intense h0l reflections. These are in good agreement with the intensity variation in the 0kl and h0l reflections of the obtained XRD diffractograms (Figure 2) [91]. The sharpness of the peaks proves that the synthesized LDHs obtained after the aging process are well crystallized.

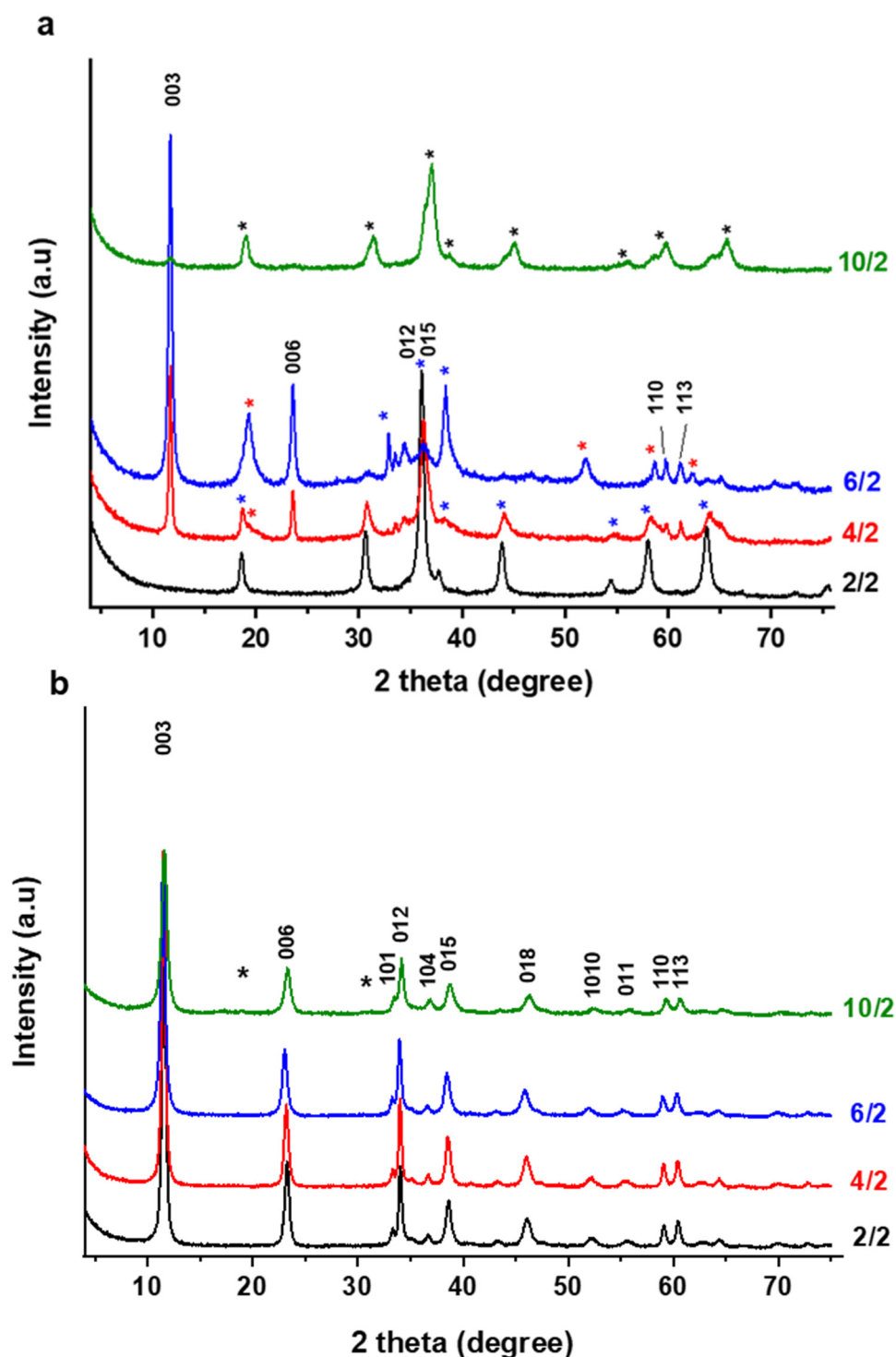


Figure 2. XRD patterns of 2/2, 4/2, 6/2, and 10/2 materials synthesized at pH values of (a) 11.5 and (b) 8.0; identified crystalline phases are: (*) $\text{Co}(\text{OH})_2$; (*) $\gamma\text{-Fe}_2\text{O}_3$; (*) Co_3O_4 .

At a co-precipitation pH value of 11.5 (Figure 2a), peaks indexed with red and blue asterisks were attributed to alpha-cobalt hydroxide ($\alpha\text{-Co}(\text{OH})_2$) (JCPDS 74-1057) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (JCPDS 83-0112) impurities, respectively, for Co/Fe ratios of 4/2 and 6/2.

Considering 10/2, traces of LDH phases were detected through the small (003) peak, while for Co/Fe 2/2, this (003) peak was not detected, clearly showing the absence of crystalline LDH phase genesis. In both products, the reflection peaks at 18.0, 30.5, 35.5, 37.0, 43.5, 53.5, 63.0, 71.5, and 75.0° (JCPDS 39-1346) are characteristic of a Co-doped maghemite

spinel structure. The 2-theta angles indicated in bold correspond to the peaks indexed with black asterisks in the diffractograms. The other peaks were missing due to the low orientation of the aggregates. This result was explained by Gregoire et al. [81], who claimed that at x values lower than 0.33 (4/2 ratio), too many M^{III} ions are present, leading to M^{III} -(O)- M^{III} interactions belonging to neighboring octahedral sites. Considering this 2/2 ratio, strong electrostatic repulsions between cations should occur and, therefore, prevent the formation of LDHs with the expected ratio. Those observed at 19.0, 31.0, 37.0, 38.5, 45.0, 56.0, and 59.5° are characteristic of an Fe-doped Co_3O_4 spinel structure (JCPDS 09-0418), which is the major phase.

According to the solids synthesized at pH 8.0 (Figure 2b), the XRD patterns exhibit characteristic reflections of LDH materials for all the investigated Co/Fe ratios. In the first descriptive approach, well-crystallized LDH phases were observed for a Co/Fe ratio lower than 10/2. For the Co/Fe 10/2 ratio, traces of cobalt-based impurity, detected at 17.0 and 19.0°, were attributed to Co_3O_4 spinel (JCPDS card No.01.080.1533). The other bands characteristic of those impurities were not detectable due to the overlaying of the Co_3O_4 characteristic bands with those of LDH phases.

In the first step, the XRD analysis of the solids synthesized at pH 8.0 and 11.5 showed that the formation of impurities is related to the pH value used during the co-precipitation method. Compared with the data obtained at pH 8.0, the high pH value (11.5) leads to the simultaneous dissolution of the previously formed LDH particles and to the reprecipitation of iron oxide and cobalt oxyhydroxide (Figure 2). Consequently, the following characterizations are focused on the Co/Fe solids, synthesized at a pH value of 8.0, which mainly comprise LDH phases.

The XRD study clearly shows that we obtained well-crystallized LDH phases synthesized at a pH value close to 8.0 for a Co/Fe ratio between 2/2 and 6/2.

Table 2 presents the full width at half maximum (FWHM) considering the 003 line, the d_{003} (Å) and d_{110} (Å), the lattice parameter ("c"), and the unit cell parameter ("a"). These were calculated from the 003 and 110 reflection positions deduced from the XRD patterns of the Co/Fe LDHs synthesized at pH 8.0 (Figure 2b). Crystallite thickness was determined from XRD data using the Scherrer equation [92].

$$L = \frac{K\lambda}{\beta \times \cos \theta}$$

where K is a shape factor constant equal to 0.89 (the value used for spherical crystallites), λ is the X-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg angle. For this study, the calculation was performed based on the diffraction peak relative to the 003 reflection.

Whatever the Co/Fe ratio, the synthesis performed at pH 8 allowed us to obtain highly pure (95 to 98%) LDH-type solids. Except for the 2/2 Co/Fe ratio, two populations of LDH phases with identical crystalline parameters and different crystallinity levels were observed through XRD quantification. In total, 21 to 28 weight % of the solid showed a very high crystallinity level, giving rise to particle sizes reaching at least 40 nm, except for the 10/2 Co/Fe ratio, which showed a mean particle size of 22 nm.

For Co/Fe ratios lower than 10/2, well-crystallized LDHs were characterized by high intensities (Figure 2b) and mean FWHM values close to 0.44° for the 003 line (values between 0.39 and 0.48 ± 0.03°; standard error related to step size used for the measurement). Consequently, the average crystallite thickness is around 180 Å, related to the stacking of about eight layers of 22.68 to 23.19 Å in depth. A less crystallized structure was observed for Co/Fe 10/2, with smaller intensities and a higher FWHM (0.61°) for the 003 line and, con-

sequently, a smaller crystallite thickness of 125 Å, related to the stacking of approximately six layers.

Table 2. Crystallographic parameters of Co/Fe LDH synthesized at pH 8.0, determined from XRD data after quantification of crystalline phases and calculated using Scherrer formula.

Co/Fe Ratio	2/2	4/2	6/2	10/2
d_{003} (Å)	7.67	7.67	7.72	7.66
d_{110} (Å)	1.55	1.56	1.56	1.56
"a" (Å)	3.12	3.13	3.13	3.12
"c" (Å)	22.90	23.01	23.19	23.00
Crystallite thickness from Scherrer formula (nm)	18 ± 1	20 ± 2	16 ± 1	13 ± 1
Full width at half maximum ± 0.03 (°)	0.44	0.39	0.48	0.61
Number of stacked layers	8	9	7	5
Mean crystallite thickness (nm)	22	17 & 47	18 & 43	11 & 22
LDH partition (%)	100	72 & 28	79 & 21	72 & 28
LDH proportion (%)	97	98	97	95

Whatever the Co/Fe ratio, the lattice parameter, "a", remains constant at 3.12 Å, in agreement with the close-enough radii values of Co^{II} (0.89 Å) and Fe^{III} (0.79 Å). These were slightly higher for Co in high-spin octahedral sites, which is the most probable energy level characteristic of cobalt in LDHs [17].

The two (00l) narrow symmetric peaks at low angles ($2\theta = 11.5$ and 23.2°) are linked to the basal spacing reflection, whose position depends on the size of the intercalated anions and their hydration state [17,93,94]. The layer-to-layer spacings in the range of 7.67 to 7.72 Å observed for the 2/2-to-10/2 Co/Fe ratios were in accordance with the presence of CO₃^{2−} as the predominant anion in the interlayer spacing [95].

The peaks appearing at a range of 55 to 65° in 2θ are characteristic of the structural organization inside the layers. Increasing the Co/Fe ratio from 6/2 to 10/2 leads to a slight shift of the 110 and 113 reflections toward higher angles, consistent with the higher Co content in the LDH structure, as high-spin octahedral Co^{II} (0.89 Å) has a larger ionic radius than Fe^{III} (0.79 Å) [17].

In the second step, the very high well-crystallized LDH contents are confirmed for all five solids elaborated from the Co/Fe solution with ratios of 2/2 to 10/2. This was accomplished using refined XRD data obtained from solids synthesized at pH 8.0 (as illustrated in Figure 3 and Figure S2 (Figures S2-1, S2-2 and S2-3), and Table 3.

The LDH type solid content was 97–98% for Co/Fe 2/2, 4/2, and 6/2 (Table 3). When using the Co/Fe solution with a 10/2 ratio, the amount of elaborated LDH reached 95%. At the same time, (Fe,Co)₃O₄ spinel contents amounted to 3.5, 0.7, and 2.3 for Co/Fe 2/2 to 6/2, while Co₃O₄ spinel content amounted to 0.7 in Co/Fe 10/2. Simultaneously, iron oxide (hematite) was not observed for Co/Fe 2/2 and did not exceed 1.5, 0.5, or 1.8%, respectively, for Co/Fe 4/2, 6/2, and 10/2. The accumulated content of secondary crystalline phases ranged from 2.2 to 5.2.

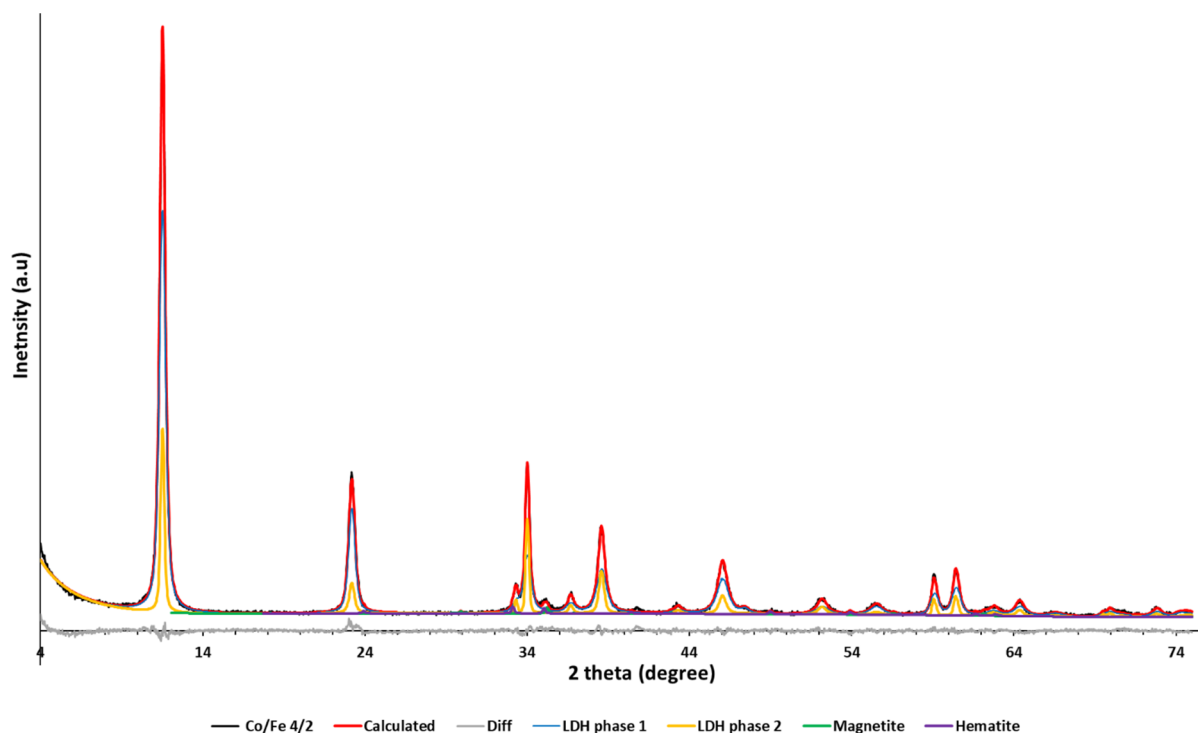


Figure 3. Rietveld refinement of Co/Fe 4/2 solid XRD patterns.

Table 3. Mineralogical composition (weight content < 3%) of solids deduced by fitting XRD patterns.

Composition (wt %)	Co/Fe Ratio			
	2/2	4/2	6/2	10/2
LDH	96.5	97.8	97.2	94.8
(Fe,Co) ₃ O ₄ /Co ₃ O ₄ , spinel for 10/2	3.5	0.7	2.3	0.7
Fe ₂ O ₃ hematite	0	1.5	0.5	1.8
β-Fe ^{III} O(OH) akaganeite	0	0	0	2.7
Total	100	100	100	100

Although Gregoire et al. [81] stated that LDH phases with cation ratios lower than 4/2 cannot be obtained, our comparison of the XRD results coupled with Rietveld refinement demonstrated the successful synthesis of 96.5% pure LDH-type solids for the 2/2 Co/Fe ratio. Additional results from physicochemical analyses will allow us to more deeply understand the crystal chemistry of the synthesized LDHs. This result can be correlated to the use of a moderate 8.0 pH value and a 60 °C aging step, which favored crystalline LDH formation compared with the 9.0 pH value co-precipitation method, followed by aging at room temperature, used by Gregoire et al. [81].

3.4. Morphological and Textural Studies of the Synthesized Co/Fe Solids

SEM and TEM analyses (Figures 4 and 5) show that the Co/Fe solids mainly exhibit the typical morphology and texture of LDHs. The SEM images (Figure 4) show that, whatever the investigated Co/Fe ratio, the LDH particles were roughly hexagonal and arranged in platelet-like sheets. This morphology results from the natural growth of well-crystallized LDHs [96].

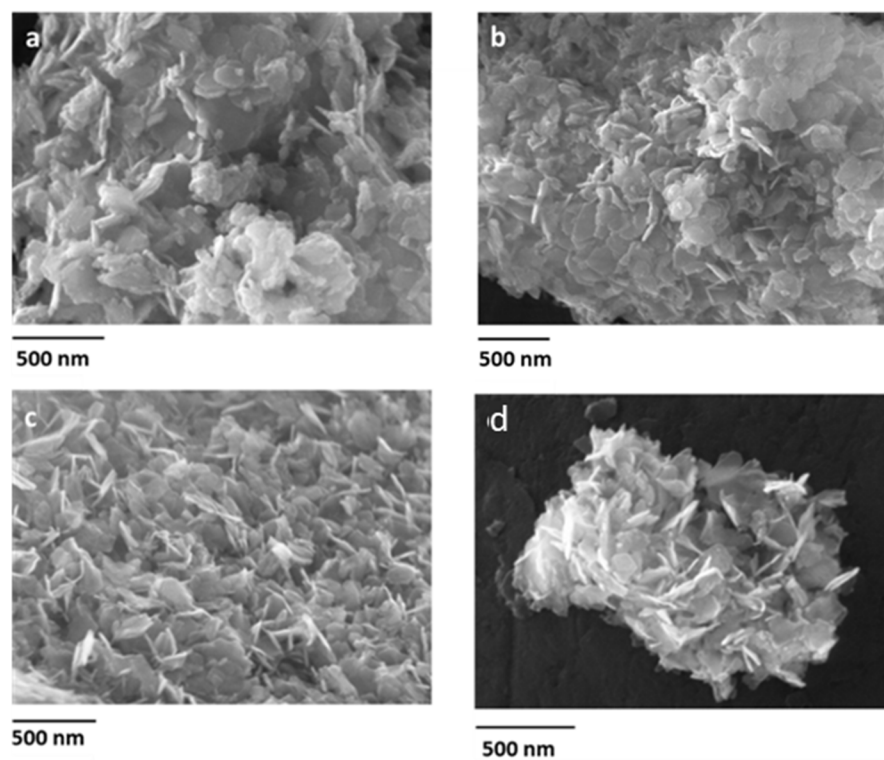


Figure 4. SEM images of Co/Fe-CO₃ LDHs: (a) 2/2, (b) 4/2, (c) 6/2, (d) 10/2.

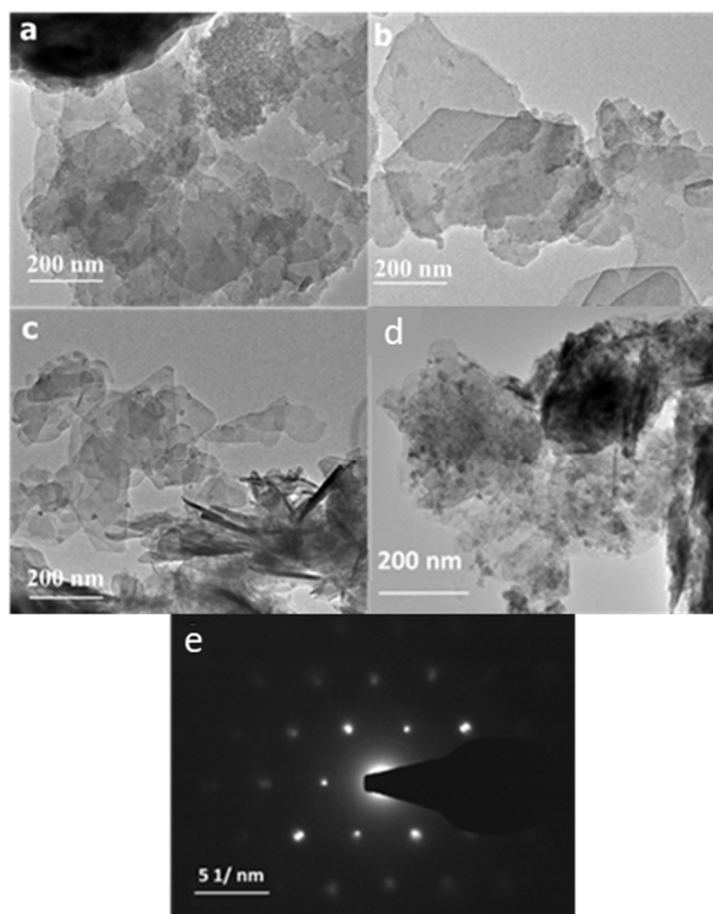


Figure 5. TEM observations of Co/Fe solids with ratios of (a) 2/2, (b) 4/2, (c) 6/2, and (d) 10/2 and (e) micro-diffraction pattern for 4/2 ratio.

The well-defined lamellar particles in the 4/2 to 6/2 Co/Fe ratios are distributed randomly with particle size (diagonal of the hexagon), ranging between 200 and 500 nm. SEM images of the 2/2 Co/Fe ratio reveal particle sizes between 1–10 nm and 400 nm, while the particle sizes of the 10/2 Co/Fe ratio range from 1–10 nm to 200 nm.

SEM images can also determine the mean thickness of ratios of 2/2 to 6/2 particles in a range of 19 to 40 nm. These values were found in the particles placed perpendicular to the observation plane. The 10/2 Co/Fe solid showed 30% thinner particle thickness (Figure 4d) compared with the others, in agreement with the higher FWHM (0.61°) determined from the XRD data (Table 2).

The TEM images (Figure 6) showed a hexagonal shape with randomly sized particles, consistent with the SEM observations. Foam-shaped platelets were mainly observed in the Co/Fe 2/2 solid.

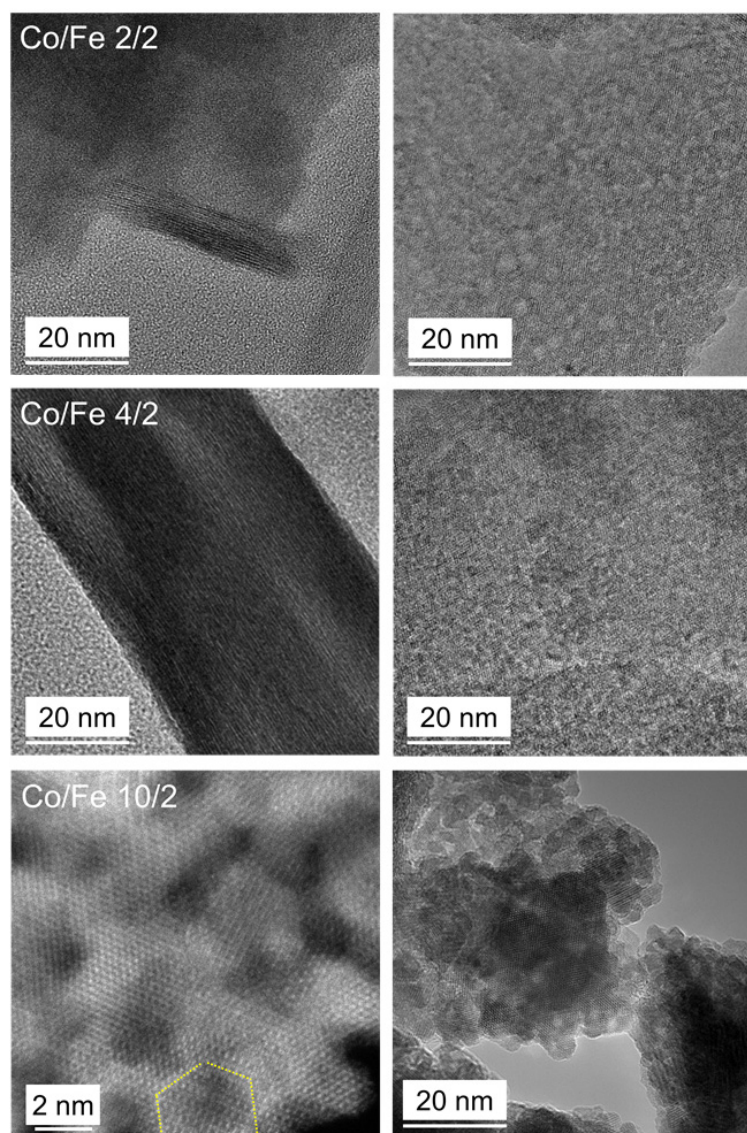


Figure 6. High-resolution TEM of Co/Fe solids with 2/2, 4/2, and 10/2 ratios showed a hexagonal shape with randomly sized particles, consistent with the SEM observations. Foam-shaped platelets were mainly observed in the Co/Fe 2/2 solid.

EDX was used on single expected LDH particles from each Co/Fe solid to better investigate the distribution of Co/Fe ratios (the results are presented in the next paragraph). Selected area electron diffraction (SAED) performed on the Co/Fe 4/2 ratio (Figure 5e)

showed *d* values of 0.258, 0.156, and 0.150 nm corresponding to the (012), (110), and (113) inter-reticular planes of the LDH crystalline structure, respectively, in agreement with XRD results.

High-resolution TEM allowed us to more deeply investigate the nanocrystallites (Figure 6). This confirmed the well-organized structure of the LDH phases, with stacking of around 15–20, 70–80, and 10–20 layers for the Co/Fe 2/2, 4/2, and 10/2 ratios, respectively. The hexagonal arrangement is visible for all compositions. This is highlighted for Co/Fe 10/2, whose image shows octahedral elementary bricks periodically arranged in hexagons.

STEM/EELS analyses of the L3/L2 ratios revealed that iron (Figure 7) is predominantly octahedral Fe^{III} (Table 4). This result is consistent with iron coordination and its redox state in LDHs under an air atmosphere. Consequently, for calculations, Fe was considered Fe^{III} in LDHs and ferrite, such as maghemite and Co/Fe spinel.

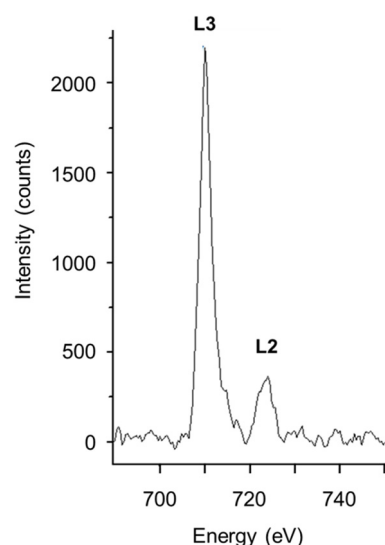


Figure 7. EELS spectrum of Fe L₃ and L₂; white lines represent Co/Fe 4/2 LDH.

Table 4. Calibration of white-line L₃/L₂ performed with Fe, FeO, Fe₂O₃, and Fe₃O₄ standards * from the literature and L₃/L₂ obtained for Co/Fe 4/2 and 6/2 LDH elaborated samples [97] **.

Iron Standards and Synthesized LDH	Mineralogical Name	Fe Redox State	Sites Geometry	White-Line L ₃ /L ₂ Relative Intensity (±0.3)
Fe *	Metallic Iron	0		3.8
FeO *	Wustite	II	Octahedral	4.6
Fe ₃ O ₄ *	Magnetite	II, III	Tetrahedral $\frac{1}{3}$ (Fe III) Octahedral $\frac{2}{3}$ (50%Fe II; 50%Fe III)	5.2
α-Fe ₂ O ₃ *	Hematite	III	Octahedral	5.8
γ-Fe ₂ O ₃ *	Maghemite	III	Tetrahedral $\frac{3}{8}$ Octahedral $\frac{5}{8}$	6.5
LDH Co/Fe 4/2 **	As-prepared LDH	III	Mainly Octahedral	5.8
LDH Co/Fe 6/2 **	As-prepared LDH	III	Mainly Octahedral	5.8

3.5. Chemical Study of Elaborated Co/Fe Solids

3.5.1. Comparative Study of Co/Fe Ratios Estimated from Bulk (AAS) and Local (EDX) Measurements

When comparing the Co/Fe experimental ratios—obtained using the AAS analysis and the expected ones based on the amount of Co and Fe salts used for the synthesis—only a slight difference was observed. The measured ratios were slightly below the expected ones, meaning that a small part of Co did not precipitate during acid–base titration (Table 5). For Co/Fe 6/2, this shift versus the expected values was 3.4% but reaches 8.7% for the 10/2 ratio.

Table 5. Comparison of data obtained by AAS from dissolved Co/Fe LDH solid suspensions and EDX from different LDH particles of each synthesized solid.

Co/Fe Ratio	Introduced Ratio	AAS Co/Fe Global Molar Ratio from Slurries ± 0.1	AAS Co/Fe Global Molar Ratio from Powders ± 0.1	EDX Co/Fe LDH Molar Ratio (Shape of Particles)	Experimental Mean Co/Fe Ratio
2/2	1.0	1.0	0.9	2.1 $\pm$ 0.2 (hexagonal) 0.7 $\pm$ 0.1 (foam)	1.1
4/2	2.0	2.0	1.8	2.0 $\pm$ 0.2 (hexagonal)	2.0
6/2	3.0	2.9	2.7	2.6 $\pm$ 0.4 (hexagonal)	2.6
10/2	5.0	4.6	4.6	3.5 $\pm$ 0.4 (hexagonal) 5.1 $\pm$ 0.2 (5 nm hexagonal particles)	4.7

For a better insight into the Co/Fe ratios, energy-dispersive X-ray analysis (EDX-TEM) was performed on individual particles of each solid to evaluate the Co/Fe ratio homogeneity. Data were compared to those acquired using AAS. The EDX analysis shows that on certain hexagonal particles, the ratio range was from 1.4 to 5.5 (Table 5). For the 2/2 introduced cation ratio, EDX showed hexagonal particles with ratios of 2.1 (4.2/2 Co/Fe LDHs) and foam-shaped particles of 0.7 (1.4/2 Co/Fe LDH), considering 3.6% of ferrite spinel ($(\text{CoFe})_3\text{O}_4$) content in the synthesized material (i.e., $n\text{Co}_{(\text{LDH})}/n\text{Fe}_{(\text{spinel}+\text{LDH})} = 0.9$). For 10/2, EDX showed co-precipitated particles with a ratio of 6/2, corresponding to 28% of LDH phases, and to a greater extent, 5 nm hexagonal LDH phases with ratios of 11/2. Akaganeite, hematite, and spinel impurities represent 5% of the solid phase. However, the 4/2 and 6/2 Co/Fe ratios are well-established in good crystalline Co/Fe LDHs (i.e., 2 for Co/Fe 4/2 and ~ 3 for Co/Fe 6/2). The limited aging period (24 h) of the suspension after co-precipitation may be responsible for cation ratios differing from those expected. A longer aging period could be required to achieve more homogenous particles in terms of cation ratios. Large and homogeneous particles were observed for the 4/2 and 6/2 ratios, leading to TEM/EDX Co/Fe ratios in agreement with the AAS analysis. When considering 2/2 and 10/2, TEM/EDX analysis was performed on the two representative LDH particle families, respectively, nanometric and pseudo-micrometric. Considering the proportion of the two LDH phases and their respective Co/Fe ratios, the experimental mean ratios are in good agreement with the AAS analysis. This result demonstrates the importance of fine TEM/EDX characterization in considering the disparity of particles to subsequently determine the chemical composition of crystalline phases.

3.5.2. Determination of Nature of Interlayer Anions

FTIR measurements were performed on solid samples to investigate the purity of the material and identify interlayer anions (Figure 8).

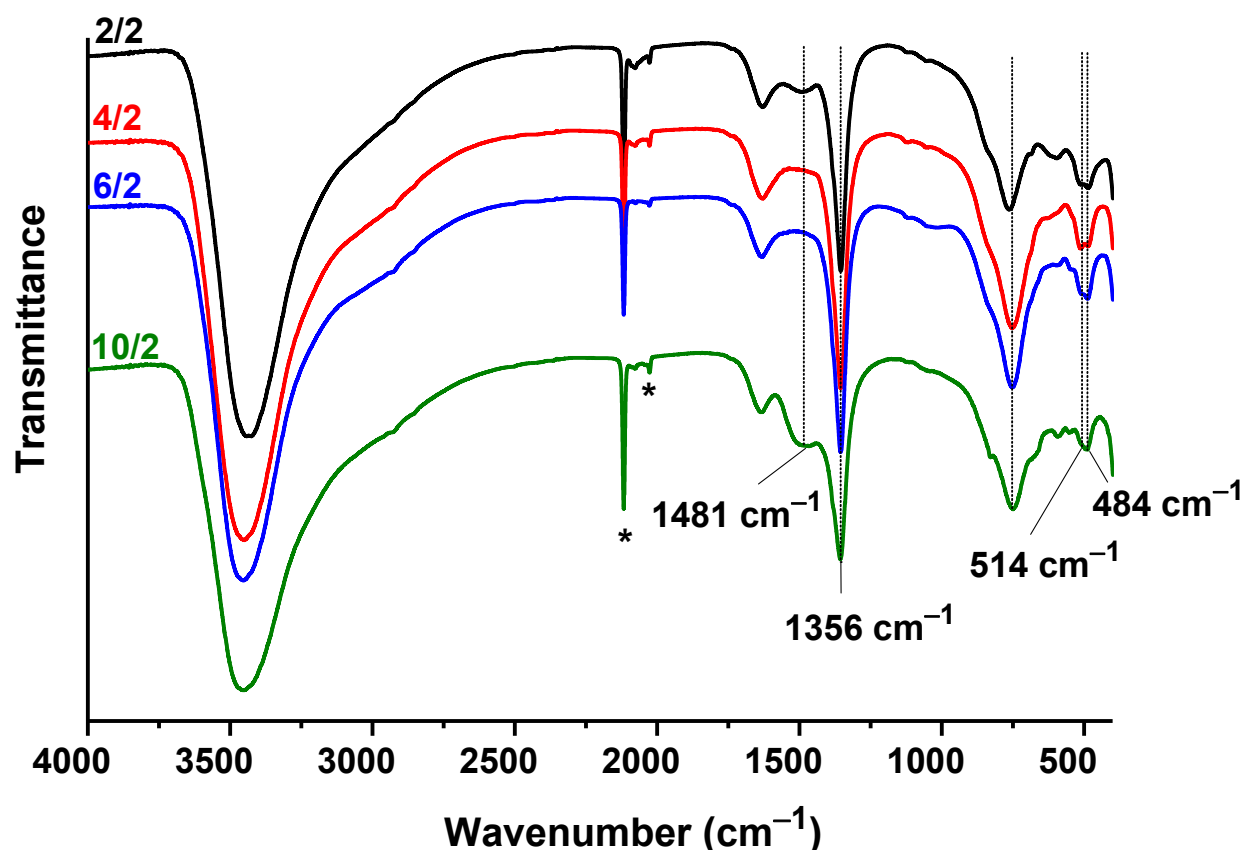


Figure 8. Overlay of Co/Fe solid FTIR spectra of Co/Fe ratios 2/2, 4/2, 6/2, and 10/2. (*) Potassium ferricyanide was added to Co/Fe solids, and its bands were used as an internal standard.

The presence of a broad band at 3450 cm^{-1} is essentially related to the O-H stretching vibrational mode of interlayered and adsorbed water molecules [18,98,99]. The bending mode band of the water molecules can be observed at 1638 cm^{-1} (Figure 8) [31,100,101]. Highlights of the FTIR spectra in the $1200\text{--}1700\text{ cm}^{-1}$, $600\text{--}1000\text{ cm}^{-1}$, and $450\text{--}600\text{ cm}^{-1}$ regions are shown in Figure 9a–c.

Carbonate anions in the interlayer space are clearly shown by the band at 1356 cm^{-1} , related to the asymmetric stretching vibration of the C-O bond of carbonates [5,13,101]. Nevertheless, the narrow band observed at 1384 cm^{-1} (Figure 9) demonstrates the presence of nitrate anions in the interlayer space [102], as traces from precursor salts remain even after the anion exchange process. At a wavenumber lower than 1000 cm^{-1} , bands at 833 cm^{-1} and 750 cm^{-1} (Figure 9) can be attributed to metal–carbonate bonds for Fe and Co, respectively [103,104].

For the Co/Fe 2/2 and 10/2 ratios, the additional presence of a wide band at 1481 cm^{-1} could be caused by HCO_3^- anions, highlighted in the literature [29]. The double band at 514 and 484 cm^{-1} can be attributed to Fe-O and Co-O bonds from the LDH structure, respectively [105]. The weak band at 544 cm^{-1} is characteristic of the Co-OH vibration mode in LDH-based materials [106].

For the 10/2 Co/Fe ratio, the band at 657 cm^{-1} can be attributed to a Co_3O_4 impurity [107], in agreement with XRD analysis. For all samples, FTIR demonstrates carbonate-based LDHs.

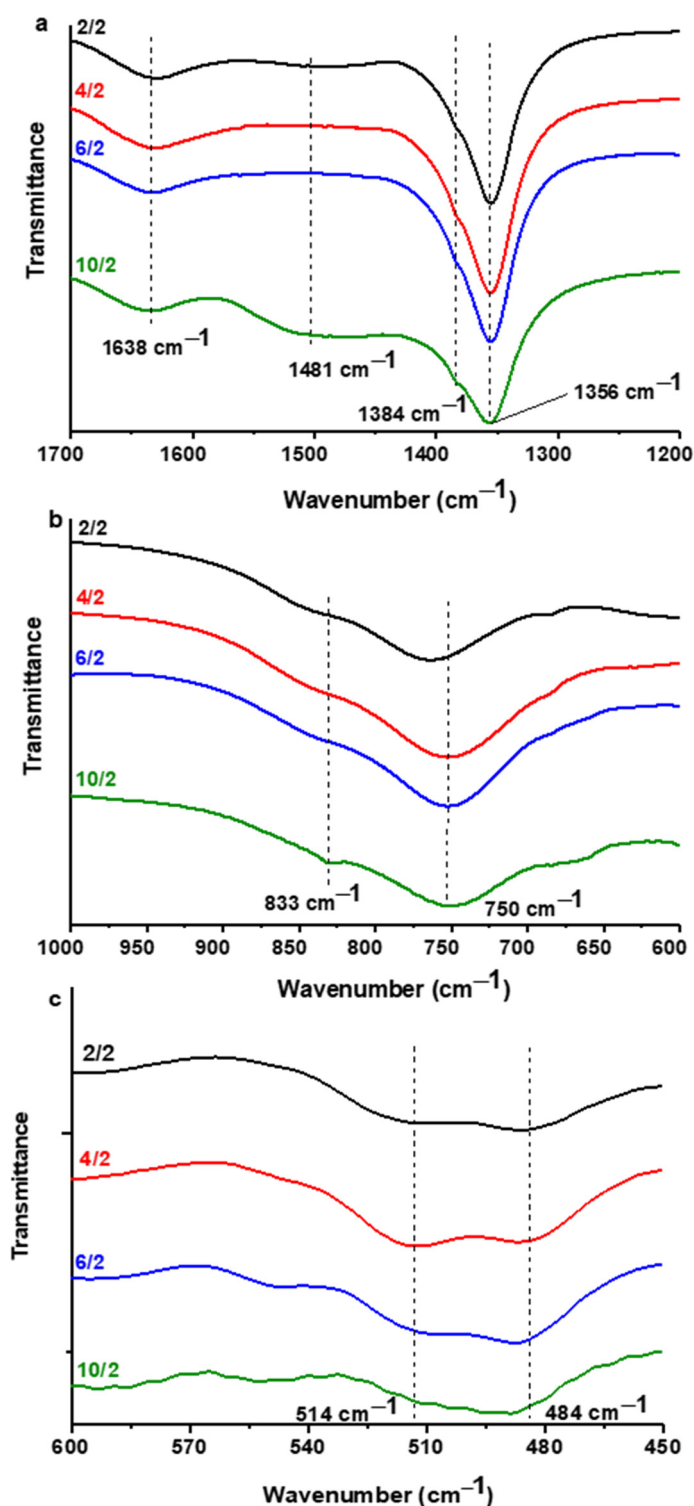


Figure 9. FTIR spectra of Co/Fe solids: highlight of interlayer anions (a,b) and structural metal-oxygen bonds (c).

3.6. LDH Chemical Formula

3.6.1. Acid–Base and Redox Reactions Involved in Mineral-Phase Formation

As demonstrated by Morcos et al. [5], ferrihydrite is the pristine reactional intermediate for Co/Fe LDH materials. Briefly, the sorption of CoII preserves the ferrihydrite-type structure in the deprotonated form of $[\text{Fe}^{\text{III}}(\text{OH})\text{O}_2]^{(2-)}-\text{Co}^{\text{II}}$, into which Fe^{III} partly reduces to Fe^{II} ; simultaneously, Co^{II} oxidizes to Co^{III} as $[\text{Fe}^{\text{III}}_{1-x}\text{Fe}^{\text{II}}_x(\text{OH})\text{O}_2]^{((2+x)-)}-(\text{Co}^{\text{II}}_{1-x}\text{Co}^{\text{III}}_x)$, into which $0 \leq x \leq 1$. This compound reacts with Co^{II} , which hydrolyzes in the solution to

form $[\text{Co}^{\text{II}}_6\text{Fe}^{\text{III}}_2(\text{OH})_{16}](\text{HCO}_3)_y(\text{CO}_3)_{1/2(2-y)}\cdot x\text{H}_2\text{O}$ LDH according to redox reactions, in agreement with the position of the redox couples on the potential scale (Figure 10).

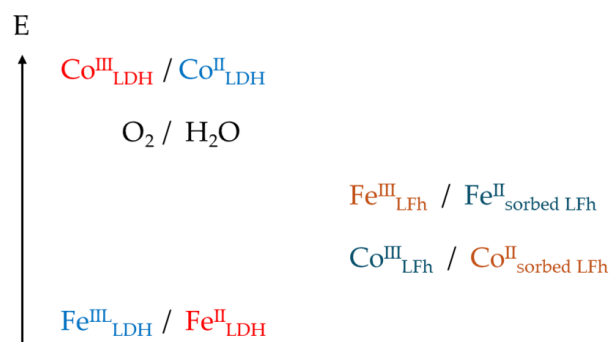


Figure 10. Positions of $\text{Co}^{\text{III}}_{\text{LDH}}/\text{Co}^{\text{II}}_{\text{LDH}}$, $\text{O}_2/\text{H}_2\text{O}$, $\text{Fe}^{\text{III}}_{\text{LFh}}/\text{Fe}^{\text{II}}_{\text{sorbed LFh}}$, $\text{Co}^{\text{III}}_{\text{LFh}}/\text{Co}^{\text{II}}_{\text{sorbed LFh}}$, and $\text{Fe}^{\text{III}}_{\text{LDH}}/\text{Fe}^{\text{II}}_{\text{LDH}}$ couples on potential scale.

The position of the $\text{Fe}^{\text{III}}_{\text{LDH}}/\text{Fe}^{\text{II}}_{\text{LDH}}$ redox couple at the bottom of the potential scale is consistent with the results reported by Duquesne et al. [34].

The placement of redox couple $\text{Co}^{\text{III}}_{\text{LDH}}/\text{Co}^{\text{II}}_{\text{LDH}}$ at the top of the potential scale is supported by electrochemical measurements performed on Co-Fe 6/2 LDHs via cyclic voltammetry. The standard potential of the $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ couple was determined as $E^\circ\text{Co}^{\text{III}}/\text{Co}^{\text{II}}\text{-Co-Fe 6/2 LDH} = 1.23 \pm 0.02 \text{ V}$ [35]. This was obtained by extrapolating measurements conducted in a pH range of 8.5–11 ($E\text{Co}^{\text{III}}/\text{Co}^{\text{II}}_{\text{Co-Fe 6/2 LDH}} = 1.231 \times \text{pH} - 0.57$). Within the investigated pH domain, $E\text{Co}^{\text{III}}/\text{Co}^{\text{II}}_{\text{Co-Fe 6/2 LDH}}$ remains higher than $E\text{O}_2/\text{H}_2\text{O}$ ($E\text{O}_2/\text{H}_2\text{O} = 1.230 \times \text{pH} - 0.60$). The reduction of Co^{III} occurs when the interfacial bulk water is oxidized. The reaction rate for Co^{III} reduction caused by H_2O is $1.3 \times 10^{-5} \text{ mol/s}$ at 25°C , which is high enough to fully reduce Co^{III} into Co^{II} within Co-Fe LDHs, further accelerated during maturation at 60°C . Accordingly, the thermodynamically stable oxidation state of Co in Co-Fe LDHs is Co^{II} .

Regarding ferrihydrite, 6LFh contains 100% Fe^{III} in an octahedral coordination [108,109]. However, upon electron-beam reduction (3×10^4 – 2.5×10^9 electrons/ nm^2), an increasing fraction of Fe^{III} migrates to tetrahedral sites. This migration is driven by the increasing electron dose, which is first likely to promote structural O^{2-} reduction. Conversely, when observed, Fe^{II} produced by the redox process remains octahedrally coordinated, thereby altering the ferrihydrite structure, which is likely to form maghemite and magnetite.

Based on Pan et al. [108], the migration of octahedral Fe^{III} of $[\text{Fe}^{\text{III}}_{1-x}\text{Fe}^{\text{II}}_x(\text{OH})\text{O}_2]^{(2+x)-} \cdot (\text{Co}^{\text{II}}_{1-x}\text{Co}^{\text{III}}_x)$ and/or the incorporation of adsorbed Co^{III} into tetrahedral sites of the ferrihydrite structure is likely to trigger maghemite and Co/Fe spinel formation once irreversibly incorporated.

Under the investigated conditions, increasing the $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ cation ratio in the reactive solution can promote the formation of finely divided ferrihydrite through sorption phenomena and, consequently, increase the amount of Fe^{III} and Co^{III} tetrahedrally coordinated in ferrihydrite during the redox process. This phenomenon likely decreases the yield of LDH-type phases by favoring the formation of $\gamma\text{-Fe}_2\text{O}_3$ and $(\text{Fe},\text{Co})_3\text{O}_4$ type impurities, in which Fe is in oxidation state III and Co is in both states II and III. According to Pan et al. [108], for an initial Co/Fe ratio of 10/2 in the precursor solution, $[\text{Fe}^{\text{III}}(\text{OH})\text{O}_2]^{(2-)}\text{-Co}^{\text{II}}$ yields $[\text{Fe}^{\text{III}}\text{O}(\text{OH})]$. Under a large excess of Co^{II} , the reductive evolution of ferrihydrite, driven by the oxidation of two Co^{II} ions, induces lattice oxygen depletion and concomitant desorption of Co.

Generally, 1.5/2 $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ LDH can be obtained in agreement with redox reactions such as $[\text{Co}^{\text{II}}_{2-x}\text{Fe}^{\text{II}}_2\text{Co}^{\text{III}}_x(\text{OH})_8](\text{HCO}_3)_y(\text{CO}_3)_{1/2(2-y)} \cdot (2\varepsilon + \varepsilon')\text{H}_2\text{O}$, which oxi-

dizes into $[\text{Co}^{\text{II}}_2\text{Fe}^{\text{III}}_2(\text{OH})_8](\text{HCO}_3)_y(\text{CO}_3)_{\frac{1}{2}(2-y)} \cdot x\text{H}_2\text{O}$. This then undergoes dissolution–reprecipitation processes. $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ 4/2 (29%) is thermodynamically favored and formed concomitantly with $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ 1.5/2 LDH (71%). The smaller particle size of $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ 1.5/2 LDH, observed by SEM and TEM analysis, can be explained by an increase in the $\text{Fe}^{\text{III}}\text{–Fe}^{\text{III}}$ interatomic distance due to repulsive interactions for a given amount of matter. Given that these phases are thermodynamically less stable, particle growth is consequently limited.

Acid–base and redox reactions are involved throughout the entire Co/Fe LDH-based synthesis process, which is further controlled by the $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio in the solution prior to precipitation and the injection pump rate through redox reaction kinetics. Compared with Morcos et al. [5], pure 97% Co/Fe 6/2 LDHs for an initial precursor solution Co/Fe ratio of 6/2 are obtained because of differences in the injection pump rate. Herein, a lower injection rate is expected to limit ferrihydrite reduction driven by Co^{II} sorption, thereby minimizing the formation of ferrite-type impurities.

3.6.2. Mineral-Phase Chemical Formula

Realistic Co/Fe LDH structures were determined using a combination of data from elemental analysis (AAS and CHON), XRD quantification, and stoichiometry determined based on local analysis (EDX-TEM), combined with the elements explained in Section 3.6.1.

Table 6 summarizes the $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ range ratios in the LDH phases and the amount of interlayered nitrate, carbonate and hydrogenocarbonate species as well as water content.

Table 6. Co/Fe range ratio in the LDH phases; corresponding carbon speciation and water content determined from elemental analyses.

Co/Fe Introduced Ratio	Chemical Formula	Weight %
2/2	$\text{Co}_{4.2}\text{Fe}_2(\text{OH})_{12.4}[(\text{NO}_3)_{0.2}, (\text{HCO}_3)_{0.8}, (\text{CO}_3)_{0.5}], (\text{H}_2\text{O})_{1.3}$	28
	$\text{Co}_{1.5}\text{Fe}_2(\text{OH})_7[(\text{NO}_3)_{0.2}, (\text{HCO}_3)_{0.8}, (\text{CO}_3)_{0.5}], (\text{H}_2\text{O})_{1.3}$	68
	Fe_2O_3	4
4/2	$\text{Co}_4\text{Fe}_2(\text{OH})_{12}[(\text{HCO}_3)_{0.06}, (\text{CO}_3)_{0.97}], (\text{H}_2\text{O})_4$	98
	CoFe_2O_4	1
	Fe_2O_3	1
6/2	$\text{Co}_{5.2}\text{Fe}_2(\text{OH})_{14.4}[(\text{NO}_3)_{0.1}, (\text{HCO}_3)_{0.3}, (\text{CO}_3)_{0.8}], (\text{H}_2\text{O})_7$	97
	$\text{Co}_{2.99}\text{Fe}_{0.01}\text{O}_4$	3
	Fe_2O_3	<1
10/2	$\text{Co}_{10.2}\text{Fe}_2(\text{OH})_{24.4}[(\text{HCO}_3)_{1.18}, (\text{CO}_3)_{0.41}], (\text{H}_2\text{O})_5$	68
	$\text{Co}_7\text{Fe}_2(\text{OH})_{18}[(\text{HCO}_3)_{1.18}, (\text{CO}_3)_{0.41}], (\text{H}_2\text{O})_{14}$	27
	Co_3O_4	<1
	Fe_2O_3	2
	$\text{FeO}(\text{OH})$	3

The calculated amounts of HCO_3^- in the interlayer region are in good agreement with the FTIR analysis spectra on which the presence of a band at 1480 cm^{-1} was observed.

Considering the 4/2 and 6/2 Co/Fe ratios, the calculated Fe/C molar ratio is close to 2, indicating that this Co/Fe LDH was mostly carbonated. Respectively, the $\text{HCO}_3^-/\text{CO}_3^{2-}$ percentages for 4/2 and 6/2 were 6/94 and 26/74. For the 2/2 and 10/2 Co/Fe ratios, the calculated Fe/C molar ratio is close to 1, indicating that hydrogen carbonate is the predominant anion within the interlayer space. Respectively, the $\text{HCO}_3^-/\text{CO}_3^{2-}$ percentages for

2/2 and 10/2 were 58/42 and 74/26. For 2/2 and 10/2, the ratio between the two HCO_3^- and CO_3^{2-} band intensity increases, in agreement with elemental analysis data.

The $d(003)$ values calculated using the XRD results (Table 2) agreed well with the mostly carbonated LDHs. For all LDHs, the presence of CO_3^{2-} in the interlayer region was confirmed by FTIR analysis, as indicated by the band observed at 1356 cm^{-1} . HCO_3^- and CO_3^{2-} coexist with variable proportions regardless of the Co/Fe cation ratio. The elemental CHON analysis allowed us to quantify nitrogen in the Co/Fe 2/2 and 6/2 samples (~ 16 and $\sim 7\%$). This confirms that the presence of nitrate, highlighted by the band observed by the FTIR analysis at 1380 cm^{-1} , was correlated with traces.

3.7. Thermal Degradation, Pore Volume, and Surface Area Study

Figure 11 and Figure S4 show the thermal behavior of Co/Fe solids investigated using TGA analysis. In agreement with [35] who investigated the thermal degradation of Co/Fe LDHs using high-temperature XRD (HTXRD) and thermogravimetric analysis coupled with gas chromatography, the TGA curves exhibited three main degradation stages, with inflection points at $140\text{--}160\text{ }^\circ\text{C}$, $205\text{--}225\text{ }^\circ\text{C}$, and $780\text{--}790\text{ }^\circ\text{C}$ [35].

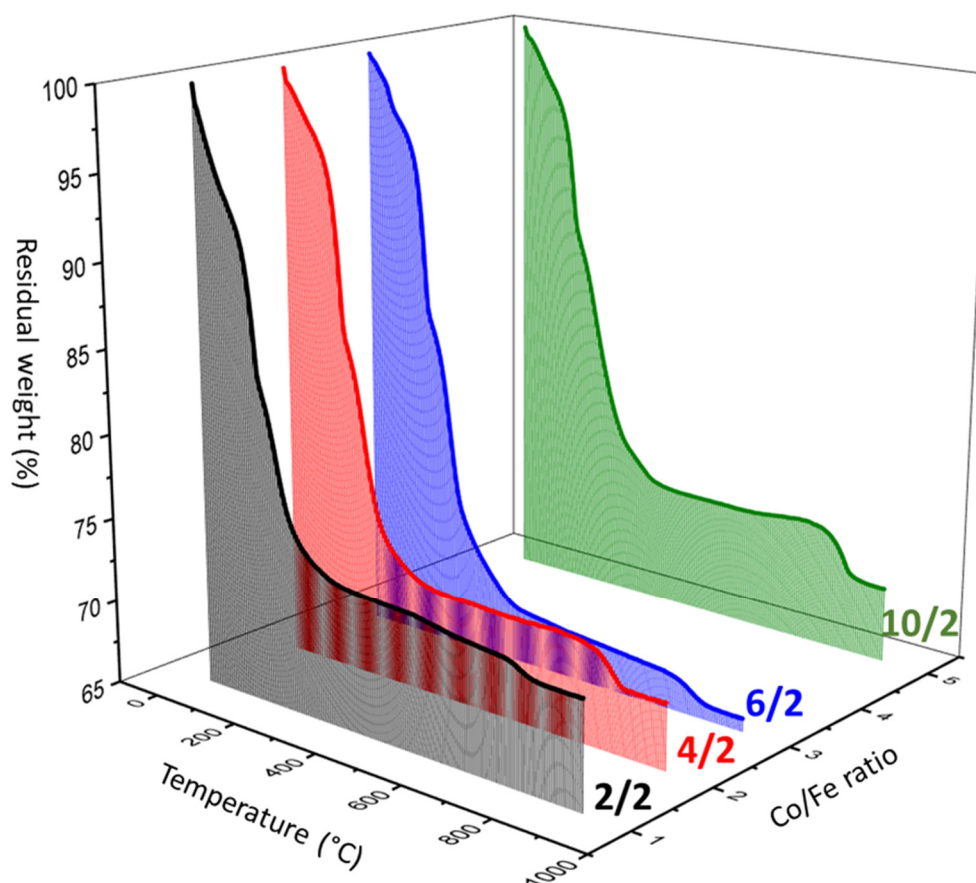


Figure 11. TGA curves of Co/Fe solids with the different cation ratios.

Except for the Co/Fe 2/2 ratio, the first stage in the range from room temperature to $140\text{--}160\text{ }^\circ\text{C}$ is essentially linked to the departure of physisorbed and interlayered water molecules. In the range from $140\text{--}160\text{ }^\circ\text{C}$ to $205\text{--}225\text{ }^\circ\text{C}$, dehydroxylation of the LDH structure occurs, as does, to a lesser extent, the possible removal of a fraction of interlayer anions [35]. In the $205\text{--}225\text{ }^\circ\text{C}$ range, the LDH transforms into an almost-amorphous spinel, while part of the CO_2 , originating from interlayer anions and adsorbed on the spinel edge oxygen atoms via chemisorption and physisorption, is released [35]. Above $205\text{--}225\text{ }^\circ\text{C}$ and up to $780\text{--}790\text{ }^\circ\text{C}$, spinel crystallization proceeds, and mass loss is related to a decrease

in residual adsorbed CO_2 . Above 780–790 °C, the mass loss is related to O departure as O_2 , creating vacancies in the spinel structure.

Regarding the Co/Fe 2/2 ratio (S4), the departure of physisorbed, interlayered water molecules and structural OH groups ranges from 20 to 165 °C. A sharp mass loss starts at 35 °C, likely due to the onset of dehydroxylation, attributable to the lability of edge hydroxyl groups in the nanometric-sized (2 nm) Co/Fe LDH (1.5/2 ratio), constituting 68% of the LDH material in the Co/Fe 2/2 sample. Dehydroxylation proceeds until 165 °C.

For cation ratios ranging from 4/2 to 10/2, the weight loss linked to physisorbed and interlayered water molecules ranged from 9 to 14%, in a temperature range of 20 to 140–160 °C. For the Co/Fe 2/2 ratio, the weight loss linked to physisorbed and interlayered water molecules is limited to 2% below 40 °C.

Dehydroxylation is responsible for 10 to 11% of weight loss. The final decomposition temperature of the LDHs (165, 205, 225, and 220 °C, respectively, for the Co/Fe 2/2, 4/2, 6/2, and 10/2 ratios) is mainly influenced by the Co/Fe cation ratio, in addition to crystallinity and morphology. Above the dehydroxylation temperature, the release of CO_2 from interlayer anions adsorbed on the edge oxygen atoms of the spinel structure is responsible for weight losses ranging from 8 to 16%. The higher weight loss of 16% observed for Co/Fe 2/2 agrees with the mass of interlamellar anions versus the mass of the LDH compounds, which are increased by interlamellar inorganic carbon speciation, i.e., 62% of HCO_3^- and 38% of CO_3^{2-} . From the 2/2 to 6/2 Co/Fe ratios, the increase in this parameter induces a decrease in the weight loss related to interlamellar anions. For Co/Fe 10/2, the measured weight loss of 8% is related to the interlamellar inorganic carbon speciation, i.e., 75% of HCO_3^- and 25% of CO_3^{2-} .

All the mass losses (Table 7) observed by TGA analyses (e.g., (i) water content originating from LDH and interlamellar, anion hydration, and structural hydroxide groups; (ii) CO_2 and, to a lesser extent, NO_2 , originating from the interlamellar anions) are correlated with the chemical formula of the predominant ($\geq 95\%$) LDH phases within the mineral phases, synthesized regardless of the Co/Fe ratios (Tables 6–8).

Table 7. Weight loss percentages at different degradation stages for various cation ratios.

Co/Fe ratio	20–40 °C (wt %)	35–165 °C (wt%)	160–785 °C (wt%)
2/2	2	11	16
Co/Fe ratio	20–145 °C (wt %)	145–205 °C (wt%)	205–785 °C (wt%)
4/2	9	11	9
Co/Fe ratio	20–160 °C (wt %)	160–225 °C (wt%)	225–785 °C (wt%)
6/2	14	10	8
Co/Fe ratio	20–140 °C (wt %)	140–220 °C (wt%)	220–785 °C (wt%)
10/2	9	11	8

Table 8. Mass of the elaborated LDH phases and their components.

Co/Fe Ratio	m (g)								
	Co	Fe	O	H	NO_3^-	HCO_3^-	CO_3^{2-}	H_2O	LDHs
2/2	248.9	223.2	310.4	19.4	24.8	97.6	60.0	46.8	1031.1
4/2	235.6	111.6	192.0	12.0	0.0	3.66	58.2	72.0	685.1
6/2	306.3	111.6	230.4	14.4	6.2	18.3	60.0	126.0	873.2
10/2	1013.1	223.2	678.4	42.4	0.0	144.00	49.2	342.0	2492.2

4. Conclusions

Solids with Co/Fe ratios between 2/2 and 10/2 were comprehensively characterized using a wide range of complementary multiscale physicochemical techniques and Rietveld refinement.

For the first time, this study demonstrates the successful synthesis of Co^{II}/Fe^{III} LDH-type materials across a broad range of cation ratios (1.5/2 to 10/2) by titrating precursor solutions with initial Co^{II}/Fe^{III} ratios between 2/2 and 10/2 up to pH 8.0. This was accomplished under the physicochemical conditions investigated above, including co-precipitation at variable pH values under atmospheric pressure, temperature, the nature and amount of alkaline reagents, and maturation temperature and duration. The cumulative mass fraction of LDH-type products consistently reaches 95–98%, while Fe and/or Co-based impurities (ferrite, hematite, and additional akaganeite for 10/2) did not exceed 5%.

Increasing the synthesis pH to 11.5 enhances the formation of impurities. At an initial solution Co/Fe ratio of 2/2, no LDH phase was formed: an 11.5 pH value promoted the formation of α -Co(OH)₂, γ -Fe₂O₃, and Co₃O₄ byproducts.

Acid–base and redox reactions are involved throughout the entire Co/Fe LDH-based synthesis process, which is further controlled by the Co^{II}/Fe^{III} ratio in the solution prior to precipitation and the injection pump rate through redox reaction kinetics. The injection rate should be high enough to maximize Co^{II} sorption while minimizing ferrihydrite reduction to minimize the formation of ferrite-type impurities.

Ferrihydrite is the pristine reactional intermediate of Co/Fe LDH materials. Co^{II} sorption preserves the ferrihydrite-type structure in the form of [Fe^{III}(OH)O₂]^(2−)–Co^{II}, into which Fe^{III} partly reduces to Fe^{II} as Co^{II} oxidizes into Co^{III} as [Fe^{III}_{1−x}Fe^{II}_x(OH)O₂]^{((2+x)−)}–(Co^{II}_{1−x}Co^{III}_x), into which 0 ≤ x ≤ 1. This compound reacts with Co^{II}, which hydrolyzes in the solution to form [Co^{II}₆Fe^{III}₂(OH)₁₆](HCO₃)_y(CO₃)_{½(2−y)} and XH₂O LDH according to redox reactions involving Co^{III}_{LDH}/Co^{II}_{LDH}, O₂/H₂O, and Fe^{III}_{LDH}/Fe^{II}_{LDH}, in agreement with the position of the redox couples on the potential scale (ECo^{III}_{LDH}/Co^{II}_{LDH} > O₂/H₂O > Fe^{III}_{LDH}/Fe^{II}_{LDH}).

The migration of octahedral Fe^{III} of [Fe^{III}_{1−x}Fe^{II}_x(OH)O₂]^{((2+x)−)}–(Co^{II}_{1−x}Co^{III}_x) and/or the incorporation of adsorbed Co^{III} into the tetrahedral sites of the ferrihydrite structure is likely to trigger maghemite and Co/Fe spinel formation once irreversibly incorporated.

Under a large excess of Co^{II}, the reductive evolution of ferrihydrite, driven by the oxidation of two Co^{II} ions, induces lattice oxygen depletion and concomitant desorption of Co.

For solids synthesized at pH 8.0, bulk chemical analysis showed that the average Co/Fe ratios closely matched the expected values; however, variations in LDH cationic ratios and morphology were observed, reflecting the coexistence of multiple LDH domains. For the first time, each LDH domain has been characterized in depth, in terms of crystalline structure, morphology, and chemical composition. The comprehensive characterization of the synthesized Co/Fe solids facilitated not only the quantification of pure LDH phases and impurities but also the determination of the LDH structure in relation to the Co/Fe ratio, Co and Fe speciation, and hydroxyl and water content. Additionally, it provided insights into the nature and speciation partition of interlamellar anions.

EDX-based local chemical analysis confirmed the formation of pure Co^{II}/Fe^{III} 98% 4/2 and 97% 6/2 LDH. For the 2/2 ratio, pure 97% LDH-type solids were distributed between Co/Fe 1.5/2 (71%) and Co/Fe 4/2 (29%). At pH 8, 1.5/2 Co^{II}/Fe^{III} LDH is generally obtained in agreement with redox reactions such as [Co^{II}_{2−x}Fe^{II}₂Co^{III}_x(OH)₈](HCO₃)_y(CO₃)_{½(2−y)}·(2ε + ε′)H₂O, which oxidizes into [Co^{II}₂Fe^{III}₂(OH)₈](HCO₃)_y(CO₃)_{½(2−y)}·XH₂O, which undergoes dissolution–reprecipitation. Co^{II}/Fe^{III} 4/2 is thermodynamically favored

and formed concomitantly with $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ 1.5/2 LDH. The smaller particle size of $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}$ 1.5/2 LDH is explained by an increase in the $\text{Fe}^{\text{III}}\text{--Fe}^{\text{III}}$ interatomic distance due to repulsive interactions for a given amount of matter. Given that these phases are thermodynamically less stable, particle growth is consequently limited. In the case of 10/2, the partial precipitation of Co was observed, inducing 95% Co/Fe LDH phases distributed between Co/Fe 10/2 (72%) and 7/2 (28%). Extending the aging time or, to a lesser extent, slightly increasing the pH above 8.0 is likely to yield a pure Co/Fe 10/2 LDH phase by promoting complete cobalt incorporation.

The layer spacing is in good agreement with predominant CO_3^{2-} anions for the 4/2 and 6/2 Co/Fe ratio LDHs, while for Co/Fe 2/2 and Co/Fe 10/2, interlayered HCO_3^- predominates. This was confirmed by FTIR spectroscopy, elemental analysis, and thermogravimetric analysis.

Multiscale characterization and analysis complemented by Rietveld refinement provided new insights into chemical co-precipitation mechanisms, enabling a deeper understanding of the formation of pure LDH-type solids.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma19050838/s1>, Pore volume and surface area determination performed via BET analysis, Rietveld refinement, and LDH chemical formula calculation. List of captions of SI [5,110]: Figure S1. Adsorption-desorption measurements of N_2 at 77 K. Figure S2-1. Rietveld refinement of Co/Fe 2/2 solid XRD patterns. Figure S2-2. Rietveld refinement of Co/Fe 6/2 solid XRD patterns. Figure S2-3. Rietveld refinement of Co/Fe 10/2 solid XRD patterns. Supplementary Information S3. LDH chemical formula calculation. Figure S4. TGA curves of Co/Fe solids with the different cation ratio.

Author Contributions: This manuscript was written with contributions from all authors. Conceptualization: S.B., S.D., F.M. and A.S. Experiments: all authors. Validation: all authors. Formal data analysis: all authors. Data curation: all authors. Writing—original draft preparation: all authors. Writing—review and editing: all authors. Visualization: all authors. Supervision: S.B., S.D., F.M. and A.S. Project administration: A.S. Funding acquisition: S.B., S.D., F.M. and A.S. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support was provided by BRGM and Région Centre Val de Loire within the framework of the SIME APR-IR project (2019–2023).

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

Acknowledgments: TGA analyses were performed by Marjorie Roulet (ICMN). F. Warmont performed the TEM and EDX analyses (MACLE-CVL).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

LDHs, layered double hydroxides; AEC, anionic exchange capacity; PZNC, Point of Zero Net Charge; XRD, X-ray diffraction; FTIR, Fourier-transform infrared SPECTROSCOPY; AAS, atomic absorption spectroscopy; TEM, transmission electron microscopy; SEM, scanning electron microscopy; EDX, energy-dispersive X-ray spectroscopy; TGA, thermogravimetric analysis; CHON, elemental analysis.

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